Spectral shape of intense exciton absorption in oligothiophene crystals

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The peculiar shape of *c*-polarized absorption spectra of crystalline oligothiophenes is attributed to the coupling between the intense upper Davydov component originating from the lowest molecular excitation and the continuum of unbound exciton-phonon states deriving from excitons off the center of the exciton Brillouin zone. This formulation is the energy-domain description of the first step of intraband exciton relaxation and, in analogy to intramolecular radiationless transitions, is couched in terms of the configuration interaction between the discrete state and the one-phonon continuum, using an exact theory originally developed by Fano. The experimental absorption shapes for individual oligothiophenes and the spectral changes along the series are very well reproduced within a unified treatment, providing a plausible explanation in terms of the interplay between the trends imposed by the changes of the exciton band width and of the effective vibronic coupling constant, with the latter parameter obtained from *ab initio* quantum chemistry calculations.

I. INTRODUCTION

Organic systems are gradually finding their way to applications in electronics and optoelectronics. Yet, the understanding of the fundamental physics underlying these applications is far from complete. This is well exemplified on the case of α oligothiophenes (nT): extensively explored with technological targets in mind,[1–4] but still offering major conceptual challenges.

Specifically, optoelectronic applications hinge upon the properties of the system's excited states, while these are not entirely understood. In oligothiophenes, the difficulties originate from the multitude of relevant excitation types and of concomitant couplings between them. Owing to the large transition dipole moment from the ground state, the Davydov splitting of the first molecular excited state is very large and, as a consequence of the crystal structure, the upper Davydov component carries an enormous share of the absorption intensity (as in H aggregates). This, on the one hand, results in its substantial interaction with the photon field, giving rise to polariton effects,[5–10] and on the other hand exposes the complex structure of lower-energy excited states. Namely, in these circumstances the vibronic replicas of the lower Davydov component are very weak and do not mask the weak absorption to charge-transfer (CT) states, so that the latter becomes an important contribution,[11,12] in contrast to the standard situation in other systems. The vibronic structure itself is rich, due to a large number of contributing modes,[13–15] and complex, because of the interplay between the intrinsic intensity carried by the lower Davydov component and the contributions borrowed from the upper Davydov component by means of a crystal equivalent of the Herzberg-Teller coupling.[16–18] These various facets of the problem have been addressed in numerous papers, both experimental[5–7,12,19] and theoretical.[11,16,17,20–22]

The feature of the oligothiophene spectra that has so far received less attention is the peculiar shape of the optical-absorption spectrum in the energy range spanned between the two Davydov components of the lowest Frenkel exciton. Apparently, the feature is common to several (presumably all) oligothiophenes.[12] The intense upper Davydov peak is preceded by a long continuous onset, starting just above the lower Davydov component. The broadening is evidently asymmetric: the high-energy tail of the upper Davydov peak is short and steep.

The provenance of the effect is not clear. At one time, it was tentatively ascribed to the strong wavelength dependence of the refraction index in the relevant energy range.[23] In our recent paper[24] we have proposed an alternative interpretation, attributing the diffuse onset to the coupling of the upper Davydov component to the continuum of unbound one-phonon states. This was based on the following argument.

By virtue of the familiar selection rule, the discrete state is optically created at zero wave vector, i.e., at the top of the exciton band which spreads far to lower energies (its width being much larger than the vibrational quantum). Inevitably, this discrete state is immersed in a continuum of two-particle states, consisting of another exciton (from the same band, but with a lower energy) and a phonon, and is coupled to those of the unbound states where the wave vectors of the two quasiparticles cancel each other. The coupling makes the discrete state prone to decay into the continuum. In time domain, this should be manifested by a shortened lifetime of the optically generated state; the broadening observed in the absorption spectrum is the energy-domain counterpart of this effect. The asymmetry of the corresponding spectral peak reflects the asymmetric disposition of the continuum with respect to the discrete state (delimited by one vibrational quantum above the bottom of the exciton band and one vibrational quantum above its top).

Accordingly, in the crystal the decay of the upper Davydov component into the unbound exciton-phonon states becomes an alternative to other pathways of its depletion, such as decay into the photon continuum, i.e., emission and relaxation into the quasicontinuum of high-energy vibrational levels of the ground electronic state, i.e., radiationless internal conversion. The new process may be viewed as an additional channel for radiationless transitions and may be treated within a similar formalism. The needed theoretical framework is readily available in the literature.[25] The problem is
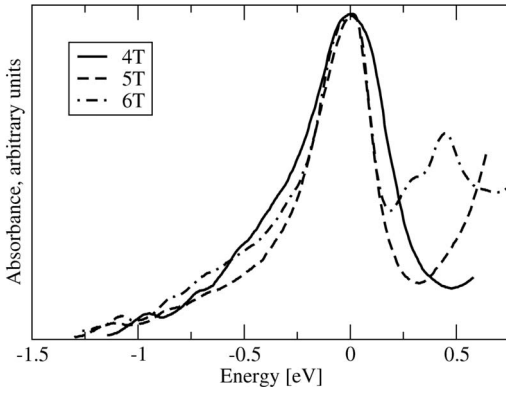
FIG. 1. Comparison between the experimental *c*-polarized absorption spectra of quaterthiophene (4T), quinquethiophene (5T), and sexithiophene (6T) (Ref. 12). The spectra are offset (in the abscissa) and scaled (in the ordinate) in such a way that their intense high-energy peaks coincide.

conveniently handled in energy domain by using the analytically solvable model proposed by Fano,[26] with a slight modification to account for the finite width of the continuum.[24]

The relevant coupling is mediated by vibronic interactions, and the corresponding coupling constant may be obtained from high-grade quantum chemistry calculations. At the time when our approach was originally conceived,[24] the needed data were available only for the bithiophene (2T) molecule and could not be directly utilized since the absorption spectrum of the corresponding crystal had not been measured. On this view, we assumed that the pertinent effects should be roughly the same for different oligothiophenes and used the 2T vibronic parameters to simulate the shape of the sexithiophene spectrum.

The recently published article[14] showed that this approximation was rather crude: although their order of magnitude remains the same, the specific values of vibronic parameters change monotonically along the oligothiophene series. The differences are rather small and it is natural to ask whether they could account for the observed differences in the experimental spectra. Figure 1 shows the spectra of the 4T–6T series shifted (along the energy axis) and scaled (in intensity) in such a way as to make the intense high-energy peak coincide. For quaterthiophene the peak is substantially broader than for the other two crystals; for 5T and 6T the shape is practically the same from the top down to about half of the peak height. Then the sexithiophene spectrum starts to deviate: there is a new band at higher energy, originating from the next intramolecular excited state, and a low-energy shoulder, probably attributable to CT states (vide infra); both features are beyond the scope of our present paper.

The ability to reproduce the difference between the spectrum of quaterthiophene and the 5T/6T spectra is a crucial test of the model presented in Ref. 24. The new results[14] offer an opportunity to perform this test by making a comparative study of the relevant systems, which should yield as a bonus a further insight into the underlying physics. This is the objective of our present paper.

II. MODEL

Specifically, we will be dealing with the crystals of 4T, 5T, and 6T (see Fig. 2). These crystals are monoclinic[27–34]
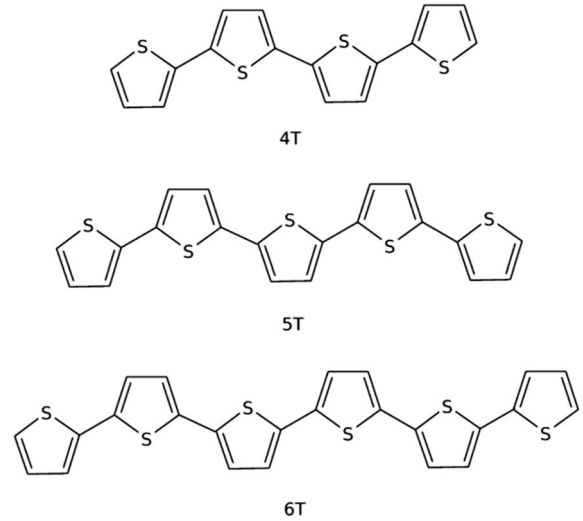

FIG. 2. Quaterthiophene, quinquethiophene, and sexithiophene molecules.

and consist of planar sheets 1 molecule thick; the projections of the molecular short axes forming a herringbone pattern (see Fig. 3). The intermolecular distances within the sheets are small (of the order of 5 Å) in contrast to the wide inter-sheet spacing; the latter is largely determined by the length of the molecule in hand, owing to the small angle between the long molecular axis and the normal to the plane of tight herringbone packing. In the low-temperature phase of the crystal the adjacent sheets are translationally nonequivalent, so that the unit cell contains four molecules, a pair from each
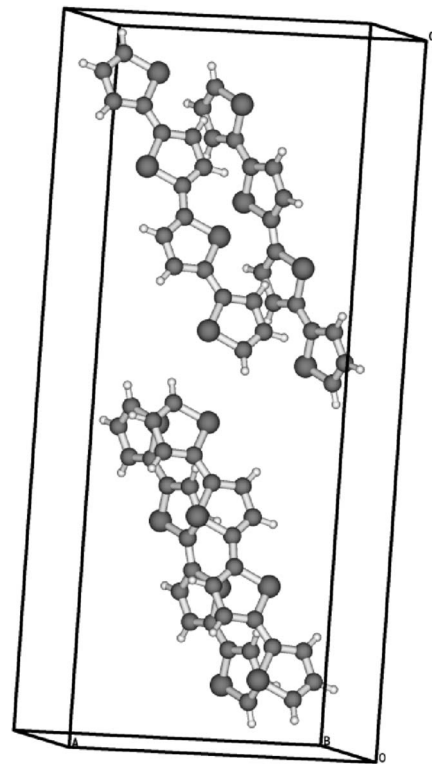

FIG. 3. Unit cell of the low-temperature phase of the quaterthiophene crystal.

of the two sheets (see Fig. 3). At high temperatures the neighboring sheets become equivalent and the unit cell is reduced to one molecular pair.

As a consequence of the large intersheet spacing, the interaction between the molecules from different sheets is very weak, producing only marginal splittings which may be safely ignored in the context of the simple generic model used in this paper. Accordingly, only two molecules per unit cell need to be explicitly included, irrespective of temperature.

Consequently, an intramolecular electronic excitation splits in the crystal into two Davydov components. As the lowest exited singlet state of the nT molecule is polarized roughly along its long axis and the long axes of the two molecules contained in the unit cell are nearly parallel, only one of the two components appears prominently in one-photon absorption. Direct calculation shows that it is the upper one, polarized along the c axis of the crystal.

As demonstrated on two-dimensional clusters,[35] this situation can be successfully mimicked within an even simpler model of a crystal with a single molecule in the unit cell. In that case the very intense upper Davydov component of the crystal with two molecules per unit cell is identified with the allowed $\mathbf{k}=0$ state of the model crystal and the lower (forbidden) Davydov component corresponds to a state at Brillouin-zone border. This simple representation is perfectly suited for our present purposes.

Then, assuming that there is one vibronically active mode per molecule, linearly coupled to the electronic excitation, the model Hamiltonian reads

$$\hat{H} = \sum_{\mathbf{m}} \epsilon B_{\mathbf{m}}^+ B_{\mathbf{m}} + \sum_{\mathbf{m}} \sum_{\mathbf{n}} W(\mathbf{n}) B_{\mathbf{m}}^+ B_{\mathbf{m+n}} + \sum_{\mathbf{m}} a_{\mathbf{m}}^+ a_{\mathbf{m}}$$
$$+ \frac{b}{\sqrt{2}} \sum_{\mathbf{m}} B_{\mathbf{m}}^+ B_{\mathbf{m}} (a_{\mathbf{m}}^+ + a_{\mathbf{m}}), \qquad (1)$$

where ϵ is the diagonal Frenkel exciton energy, $W(\mathbf{n})$ denotes the exciton resonance integrals, b is the dimensionless Franck-Condon parameter (exciton-phonon coupling constant) while $B_{\mathbf{m}}$ and $a_{\mathbf{m}}$ are the exciton and phonon annihilation operators, respectively. For phonons the Einstein model is adopted (i.e., they are assumed to be dispersionless) and all energies are expressed in terms of their vibrational quantum $\hbar\omega$.

The propagation part of the above Hamiltonian is readily diagonalized by the Fourier transformation

$$B_{\mathbf{m}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{km}} B_{\mathbf{k}}, \qquad (2a)$$

$$B_{\mathbf{m}}^+ = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{km}} B_{\mathbf{k}}^+, \qquad (2b)$$

$$a_{\mathbf{m}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{-i\mathbf{qm}} a_{\mathbf{q}}, \qquad (2c)$$

$$a_{\mathbf{m}}^+ = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{qm}} a_{\mathbf{q}}^+, \qquad (2d)$$

where N is the number of molecules in the crystal. The transformed Hamiltonian assumes the form

$$\hat{H} = \sum_{\mathbf{k}} [\epsilon + W(\mathbf{k})] B_{\mathbf{k}}^+ B_{\mathbf{k}} + \sum_{\mathbf{q}} a_{\mathbf{q}}^+ a_{\mathbf{q}}$$
$$+ \frac{b}{\sqrt{2N}} \sum_{\mathbf{k}} \sum_{\mathbf{q}} B_{\mathbf{k}}^+ B_{\mathbf{k-q}} (a_{-\mathbf{q}}^+ + a_{\mathbf{q}}). \qquad (3)$$

As was shown previously,[24] the only states relevant in the present context are $|\phi(\mathbf{k}=0)\rangle |0\} = B_0^+|0\rangle |0\}$ (which lends the absorption intensity) and $|\phi(\mathbf{k})\rangle |-\mathbf{k}\} = B_{\mathbf{k}}^+|0\rangle a_{-\mathbf{k}}^+ |0\}$ (which borrow the intensity and give rise to line broadening), where the pointed and wavy brackets refer to the exciton and phonon states, respectively; the corresponding vacuum states are denoted $|0\rangle$ and $|0\}$.

In all crystals under consideration the Davydov splitting is much larger than the vibronic coupling constant and the vibrational quantum, which suggests that a perturbative treatment based on the strong intermolecular (weak vibronic) coupling limit should be a reasonable approximation. Specifically, with respect to the upper Davydov component this view is corroborated by the numerical results obtained for finite clusters[36] as well as for an infinite crystal:[37,38] the corresponding eigenstate turns out to be practically a free Frenkel exciton. The displacement of the equilibrium position upon electronic excitation is distributed over a very large number of molecules, while at an individual molecule the lattice distortion is minuscule. This spread of the distortion in coordinate space indicates that the vibrational modes in the excited electronic state are best viewed as delocalized phonons not bound to the exciton, which is just the picture obtained when the Born-Oppenheimer approximation is applied to the crystal as a whole, i.e., in the weak vibronic coupling limit.

However, one should bear in mind that the existing formulations,[17,18,20–22,35,36] constructed in a finite basis set consisting of localized functions, are poorly suited to describe the vibrational excitations of this kind, since any finite subset of localized states constitutes only a negligible fraction of the total number of the corresponding states in an infinite crystal. This deficiency is remedied by using the approach we have recently proposed,[24] where the weak vibronic coupling of the upper Davydov component at $\mathbf{k}=0$ to unbound one-phonon states composed of the exciton with wave vector $\mathbf{k}$ and a phonon with wave vector $-\mathbf{k}$ is treated in terms of configuration interaction between a discrete state and a continuum, proposed by Fano[26] and subsequently applied by Bixon and Jortner[25] to describe radiationless transitions.

III. CALCULATIONS AND RESULTS

In our recent paper[24] we have adapted the Fano approach (for intramolecular radiationless transitions employed in its original form[25]) to account for the finite width of the exciton-phonon continuum and for its actual disposition with respect

to the intense discrete state. The details of the derivation may be found there; here we merely cite the final formula for the energy dependence of absorption intensity

$$I(E) = \frac{N\mu^2 b^2}{4C} \frac{1}{\left(E - E_\phi - \frac{b^2}{4C}\ln\left(\frac{|E - \alpha|}{|E - \beta|}\right)\right)^2 + \frac{\pi^2 b^4}{16C^2}}$$
$$\times \frac{1}{\frac{1}{\pi}\arctan\left(\frac{4C(\beta - E_\phi)}{\pi b^2}\right) - \frac{1}{\pi}\arctan\left(\frac{4C(\alpha - E_\phi)}{\pi b^2}\right)},$$
$$(4)$$

where μ is the molecular transition dipole moment, $2C$ is the width of the exciton band (in the present approach identified with the experimental Davydov splitting), E_ϕ stands for the energy of the $\mathbf{k}=0$ discrete state, while α and β delimit the energy range of the continuum in which this state is immersed.

The above formula is based on the additional approximation of constant density of states (DOS) within the exciton band, which is admittedly simplistic but inevitable as long as analytical solutions are to be found. Account taken of other simplifications of the model, and in view of the low resolution of the spectra to be interpreted, this does not seem to be a serious limitation. However, the discontinuity at band edges, where DOS changes abruptly from zero to a finite value, in the absorption intensity of Eq. (4) gives rise to mild (logarithmic) singularities. This problem is circumvented by confining the calculations to the interval (α, β), slightly narrower than the actual exciton band width $2C$. In practical terms, the calculations (that are done numerically anyway) stop two quadrature points short of the exact band-edge energy, which introduces only a marginal error.

Each point of the curve defined by Eq. (4) represents an optical transition to a group of states at energy E and is expected to have some intrinsic spectral width, partly radiative and partly due to other factors, such as, e.g., intramolecular radiationless transitions and inhomogeneous broadening. In our approach this fact is taken into account by dressing the corresponding spectral line in a Lorentzian curve characterized by the width Γ; the actual absorption spectrum is numerically calculated as the convolution of the envelope of Eq. (4) with the Lorentzian shape function. The width of this latter function is assumed to be the same for all oligothiophenes and equal 0.004 eV; within reasonable limits, its precise value barely affects the resultant absorption profile, which is then governed by only two parameters (C and b).

For sexithiophene, the calculated Davydov splitting (here corresponding to $2C$) depends on the adopted approximations and on the molecular transition dipole moment,[2,39,40] the latter considerably differing between different experimental reports. Therefore, in the present approach we use the specific values known from experiment for individual oligothiophene crystals[12] and listed in Table I.

The vibronic coupling constant b in Eqs. (1), (2a)–(2d), and (3) refers to a specific vibrational mode. The mode that couples most strongly to electronic excitation is a ring stretch

TABLE I. The values of Davydov splitting ($2C$) and effective coupling constant with (b^{eff}) and without polariton effects ($b^{\#}$).

Compound	$2C$ (eV)	$b^{\#}$	b^{eff}
4T	0.97	1.41	1.9
5T	1.13	1.35	1.8
6T	1.09	1.27	1.7

of about 1450 cm^{-1} (0.18 eV), but in reality the molecule has more than one normal vibration and in the crystal all of them form independent continua. Fortunately, according to Fano,[26] the spectral consequences of the interaction with several continua closely resemble those for a single continuum, the only difference being that the shape of the absorption spectrum is then governed by the sum of the squares of the relevant coupling constants instead of a single coupling constant. This result may be mimicked within the single-continuum approximation if the mode under consideration is treated as an effective one, with the coupling constant representing the total vibronic relaxation energy (Stokes shift) of the molecule, according to the formula

$$b^{\#} = \sqrt{\sum_i b_i^2 \frac{\omega_i}{\omega}}, \qquad (5)$$

where the summation runs over all the normal modes of the molecule, b_i and ω_i, denoting their distortion parameters and frequencies. ω is the frequency of the representative mode, defining the energy unit in Eq. (1); of course, the results do not depend on its choice.

The vast body of needed input information has recently been published by Andrzejak and Pawlikowski.[14] Their DFT/TDDFT calculations with the B3LYP potential were performed in the triple zeta valence quality (TZVP) basis, expected to yield reasonably accurate distortion parameters. The resultant values of the effective coupling constant $b^{\#}$ for 4T, 5T, and 6T are listed in Table I.

The above approach has some obvious deficiencies, absent in the situation originally considered by Fano. In the present case, the continua do not extend to infinity. For each individual mode the continuum starts at a somewhat different energy, corresponding to the lower edge of the exciton band increased by one quantum of the specific mode in hand. In a more realistic model, the single stepwise onset at low energies should turn into a set of steps, shifted with respect to each other by intervals representing the differences in mode frequencies; the finite width of the absorption contributions from individual states would smear them out to produce a steep but essentially smooth curve. The same would apply to the stepwise cutoff at high energies, further improving the agreement with experimental spectra.

Another shortcoming of our approach is more fundamental, but ultimately not very disturbing. Because of its enormous oscillator strength, the upper Davydov component of oligothiophene crystals strongly couples to the photon field, giving rise to polariton resonances.[5–7] Fortunately, the spec-
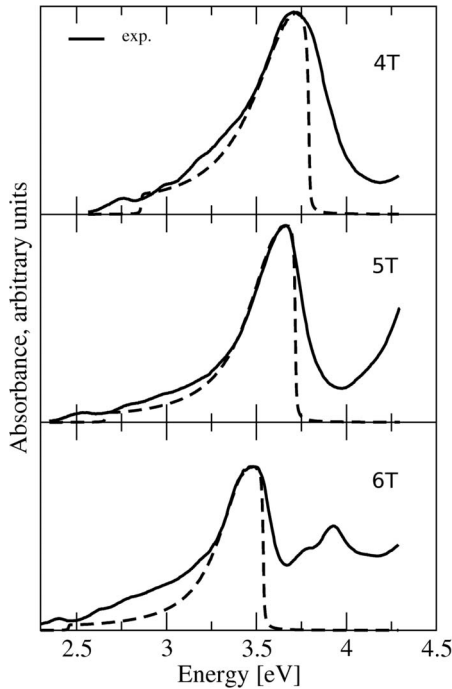
FIG. 4. Calculated (broken line) vs experimental (Ref. 12) (solid line) absorption spectra of oligothiophenes.

tral consequences of this interaction are not as dramatic as originally supposed: the corresponding absorption peak is somewhat broadened, marginally shifted to the blue[8] and slightly distorted on the high-energy side. While consistent incorporation of polariton effects in our approach would be a formidable task, their main impact may be simulated by phenomenologically increasing the width of the calculated spectral profile, i.e., by adding a polariton contribution δ to the effective coupling constant $b^{\#}$ governing the width

$$b^{\mathrm{eff}} = b^{\#} + \delta. \qquad (6)$$

The correction δ depends primarily on the oscillator strength of the transition in hand, which is practically the same for all the compounds under consideration. This enables us to use in all cases the same value, originally obtained for 6T by comparing a hypothetical purely excitonic spectrum with the calculated polaritonic one.[8] Converted to the vibrational quantum units of the present paper, it amounts to 0.45. The modified values of the effective coupling constant b^{eff} for 4T, 5T, and 6T are listed in Table I and the calculated spectra are shown in Fig. 4, along with their experimental counterparts.

IV. DISCUSSION

In view of the simplicity of the applied model and of the fact that no fitting parameters are used to reproduce the individual spectra, the agreement with experiment is excellent. In all cases the shape of the low-energy side of the main absorption peak, starting from about 3.2 eV, is perfectly rendered. The discrepancies are readily attributable to identifiable approximations. The experimentally observed weak band at the low-energy end of the spectrum is due to

Herzberg-Teller-type intensity borrowing from the upper Davydov component by vibronic replicas of the lower Davydov component, mediated by low-energy vibrations.[16–18] These effects, ascribed to bound exciton-phonon states, have already been plausibly interpreted within a sophisticated approach valid in the regime of intermediate vibronic coupling.[17,18] They engage only a small spatial region in the close neighborhood of the exciton and negligibly affect the extended unbound states treated in the present paper, although they do carry a perceptible fraction of the total intensity. Their contributions appear also at higher energies, but in that particular range are dominated by those from the unbound states.

The reproduction of the low-energy part of the spectrum is the least satisfactory for 6T. It is our conjecture that, apart from the effects discussed above, these discrepancies are due to the contributions from CT states. The CT states prevail in the sexithiophene electroabsorption spectrum. Owing to some energetic peculiarities,[41] in quaterthiophene, CT absorption is located closer to the upper Davydov component of the Frenkel state, in agreement with the energy range where the calculated curve deviates most strongly from the experimental spectrum.

The discrepancies at the high-energy side of the intense maximum may be partly due to the spread in the cutoff energies of the continua for different vibrational modes, but are predominantly attributable to the line-shape perturbation resulting from polariton effects, as demonstrated in the past.[8] Another contribution, especially prominent for 6T, comes from higher excited states of the molecule.

Overall, the observed shape of the oligothiophene absorption profile may be affected also by other factors, such as some inhomogeneous broadening due to defects and thermally populated levels; also some contribution from the losses due to the strong wavelength dependence of the refraction index in the relevant energy range[23] cannot be ruled out. On this view, one should not be overly impressed by the quantitative agreement of the present results with experimental spectra. In our opinion, the success in reproducing both the common features of the spectra and the trend along the oligothiophene series is much more important. The striking qualitative similarity between the line shapes observed for different oligothiophenes is consistent with the analogies in their molecular and crystal structure. Yet, when their spectra are directly compared, also the differences become visually evident. They can be rationalized in terms of the interplay between the Davydov splitting and the effective constant $b^{\#}$ that governs the coupling of the discrete state to the continuum.

According to Eq. (4), the value of the coupling constant directly translates into the width of the observed absorption peak. A smaller Davydov splitting implies a larger density of states in the exciton band, facilitating the decay of the discrete state and also enhancing its width. In quaterthiophene both ingredients concur in broadening the observed peak (cf. Table I). The somewhat wider exciton band is responsible for the narrower absorption peaks of 5T and 6T; the difference on this account between the two crystals is to a large extent compensated by the reversed trend in the coupling constants.

As noted by Fano, $\tau = \frac{2\hbar C}{\pi b^2}$ should represent the mean lifetime of the discrete level embedded in the continuum. In the

present context, this would be strictly true if the calculated absorption curve was a complete Lorentzian; in reality, it is (asymmetrically) truncated at the sides. In time domain, this is expected to produce nonexponential contributions to the decay and probably some increase of the actual lifetime with respect to the above crude estimate.

In our present case the decay is tantamount to intraband relaxation or, strictly speaking, to the initial stage thereof. In course of subsequent evolution, the excitons created at $\mathbf{k} \neq 0$ further dissipate their excess energy to reach ultimately the minimum, in our model located at the border of the Brillouin zone, and in the actual crystal corresponding to the lower Davydov component.

Account taken of the notorious sensitivity of calculated rate constants to even minor shortcomings of the underlying theoretical description, it would be exceedingly optimistic to expect our simplistic model to yield precise temporal predictions. Nevertheless, it does seem encouraging that the estimate of about 3–4 fs, based on the calculated b^{eff} values, is compatible with the relaxation times (50-150 fs) measured by pump-probe experiments of Engel *et al.*[42,43] for PTCDA (perylene-3,4,9,10 -tetracorboxylic -3,4,9,10 -dianhydride) and MePTCDI [N,N-dimethylperylene-3,4:9,10-bis(dicarboimide)]. If the experimental results obtained for an entirely different system may be relied upon in the present context and if our estimate may be taken at face value, the decay of the discrete state into the continuum is not the rate-determining step of the intraband relaxation process, which is not surprising. Unfortunately, the existing article on the subject,[44] referring specifically to sexithiophene, does not cover the relevant energy range. Pump-probe experiments with extremely high temporal and energetic resolutions might shed new light on the problem. We hope that the present paper will inspire such a study.

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[1] *Handbook of Conducting Polymers*, edited by T. A. Scotheim (Marcel Dekker, New York, 2007), Vols. 1 and 2.

[2] *Handbook of Oligo- and Poly-Thiophenes*, edited by D. Fichou (Wiley, Weinheim, 1999).

[3] G. Horowitz, D. Fichou, X. Peng, Z. Xu, and F. Garnier, Solid State Commun. **72**, 381 (1989).

[4] A. Dodabalapur, L. Torsi, and H. E. Katz, Science **268**, 270 (1995).

[5] S. Möller and G. Weiser, Synth. Met. **122**, 41 (2001).

[6] G. Weiser and S. Möller, Phys. Rev. B **65**, 045203 (2002).

[7] G. Weiser and S. Möller, Org. Electron. **5**, 91 (2004).

[8] A. Stradomska and P. Petelenz, Acta Phys. Pol. A **112**, S161 (2007).

[9] A. Stradomska and P. Petelenz, Org. Electron. **7**, 551 (2006).

[10] P. Petelenz and A. Stradomska, Phys. Rev. B **71**, 235205 (2005).

[11] M. Andrzejak, P. Petelenz, M. Slawik, and R. W. Munn, J. Chem. Phys. **117**, 1328 (2002).

[12] S. Tavazzi, M. Laicini, L. Raimondo, P. Spearman, A. Borghesi, A. Papagni, and S. Trabattoni, Appl. Surf. Sci. **253**, 296 (2006).

[13] M. Muccini, E. Lunedei, A. Bree, G. Horovitz, F. Garnier, and C. Taliani, J. Chem. Phys. **108**, 7327 (1998).

[14] M. Andrzejak and M. Pawlikowski, J. Phys. Chem. A **112**, 13737 (2008).

[15] J. Gierschner, H.-G. Mack, H.-J. Egelhaaf, S. Schweizer, B. Doser, and D. Oelkrug, Synth. Met. **138**, 311 (2003).

[16] P. Petelenz and M. Andrzejak, J. Chem. Phys. **113**, 11306 (2000).

[17] Z. Zhao and F. C. Spano, J. Chem. Phys. **122**, 114701 (2005).

[18] F. C. Spano, L. Silvestri, P. Spearman, L. Raimondo, and S. Tavazzi, J. Chem. Phys. **127**, 184703 (2007).

[19] L. Raimondo, M. Laicini, S. Tavazzi, A. Borghesi, and P. Spearman, J. Chem. Phys. **122**, 064706 (2005).

[20] A. Stradomska and P. Petelenz, J. Chem. Phys. **130**, 094705 (2009).

[21] F. C. Spano, J. Chem. Phys. **116**, 5877 (2002).

[22] Z. Zhao and F. C. Spano, J. Phys. Chem. C **111**, 6113 (2007).

[23] H.-J. Egelhaaf, J. Gierschner, J. Haiber, and D. Oelkrug, Opt. Mater. **12**, 395 (1999).

[24] P. Petelenz and W. Kulig, Chem. Phys. **343**, 100 (2008).

[25] M. Bixon and J. Jortner, J. Chem. Phys. **50**, 3284 (1969).

[26] U. Fano, Phys. Rev. **124**, 1866 (1961).

[27] D. Fichou, J. Mater. Chem. **10**, 571 (2000).

[28] M. Pelletier and F. Brisse, Acta Crystallogr. C: Cryst. Struct. Commun. **50**, 1942 (1994).

[29] F. van Bolhuis, H. Wynberg, E. E. Havinga, E. W. Meijer, and E. G. J. Starring, Synth. Met. **30**, 381 (1989).

[30] T. Siegrist, C. Kloc, R. A. Laudise, H. E. Katz, and R. C. Haddon, Adv. Mater. (Weinheim, Ger.) **10**, 379 (1998).

[31] L. Antolini, G. Horovitz, F. Kouki, and F. Garnier, Adv. Mater. (Weinheim, Ger.) **10**, 382 (1998).

[32] G. Horovitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J. L. Fave, and F. Garnier, Chem. Mater. **7**, 1337 (1995).

[33] T. Siegrist, R. M. Fleming, R. C. Haddon, R. A. Laudise, A. J. Lovinger, H. E. Katz, P. Bridenbaugh, and D. D. Davis, J. Mater. Res. **10**, 2170 (1995).

[34] D. Fichou, B. Bachet, F. Demanze, I. Billy, G. Horovitz, and F. Garnier, Adv. Mater. (Weinheim, Ger.) **8**, 500 (1996).

[35] F. C. Spano, J. Chem. Phys. **120**, 7643 (2004).

[36] F. C. Spano, J. Chem. Phys. **118**, 981 (2003).

[37] A. Stradomska, Ph.D. thesis, Jagiellonian University, 2008.

[38] A. Stradomska and P. Petelenz (unpublished).

[39] M. Muccini, E. Lunedei, C. Taliani, D. Beljonne, J. Cornil, and J. L. Brédas, J. Chem. Phys. **109**, 10513 (1998).

[40] P. Petelenz and M. Andrzejak, Chem. Phys. Lett. **343**, 139 (2001).

[41] P. Petelenz, M. Slawik, and W. Kulig, Phys. Status Solidi C **6**, 85 (2009).

[42] E. Engel, M. Koschorreck, K. Leo, and M. Hoffmann, J. Lumin. **112**, 299 (2005).

[43] E. Engel, Ph.D. thesis, Technische Universität Dresden, 2005.

[44] S. V. Frolov, C. Kloc, B. Batlogg, M. Wohlgenannt, X. Jiang, and Z. V. Vardeny, Phys. Rev. B **63**, 205203 (2001).